Pilot Testing of Technologies to Treat Multiple Contaminants in Drinking Water at the Pine Hill School on the Ramah Navajo Reservation:

A Collaborative Project between the Navajo Nation EPA and Sandia National Laboratories

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14th Annual Tribal EPA Conference
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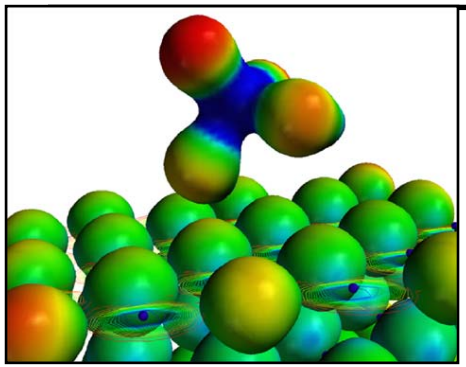
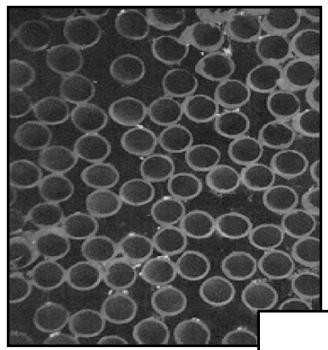
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

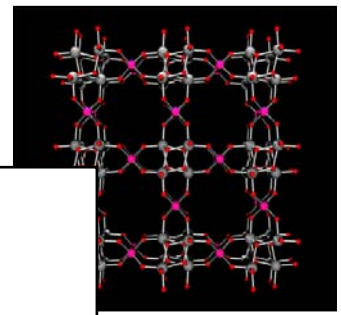
Sandia National Laboratories and Drinking Water



Cost-effective contaminant removal technologies



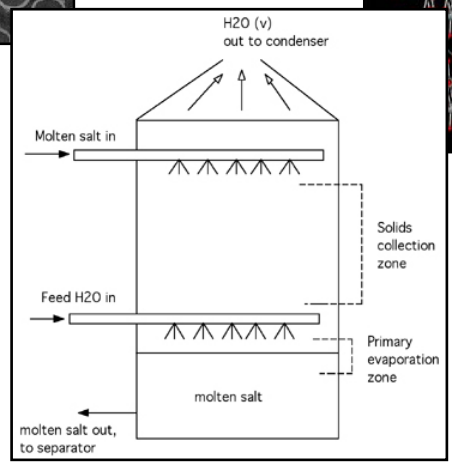
Next-generation desalination technologies



Design of chemical filter materials

Pervaporation

In situ crystallization



Integrated chem/bio treatment technologies

Point of use (rather than centralized) treatment technologies

Direct contact distillation

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Arsenic Water Technology Partnership

- **Congressional Appropriation - $13M for FY03-FY06**
- **DOE- funded peer-reviewed, cost-shared research program to develop and demonstrate innovative technologies for removal and disposal of arsenic from drinking water.**
- **Partners**
  - **Bench-Scale Studies (AwwaRF)**
  - **Demonstration Studies (Sandia)**
  - **Economic Analysis/Outreach (WERC)**
- **Focus on small systems**
  - **40% of resources directed to rural and Native American utility needs**
  - **Minimize costs - capital, operating, maintenance**
  - **Minimize residual quantities & disposal costs**

Question: What advances in treatment technology can significantly reduce costs of treating multiple contaminants?

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Acknowledgements

- Ramah Navajo School Board
- Ron Francis, Dominic Maria, Steve Garcia (Pine Hill)
- Dariel Yazzie, Yolanda Barney (NNEPA)
- Kathleen Holt; Malynda Aragon, Randy Everett, William Holub Jr., Carolyn Kirby, Michelle Shedd, Andres Sanchez, Rose Preston, Joe Zigmond, Jen Ashley, Pam Puissant, Tom Hinkebein, Pat Brady, Richard Kottenstette (SNL)
- AwwaRF partners
- WERC partners

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Outline

- **Background:**
  - **Significance of multiple naturally-occurring contaminants in drinking water sources**
- **Description of Pine Hill School site**
- **Pilot Test**
  - **Objectives**
  - **Treatment technologies**
  - **Pilot skid design**
- **Preliminary Results**
- **Proposed workshop on Technologies for non-PWS users**

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Background

- **Recent reduction of drinking water Maximum Concentration Level (MCL) for arsenic from 50 ppb to 10 ppb (January 2006) was intended to reduce incidence of bladder cancer and other cancers in US.**
- **Southwestern United States is characterized by high and variable background levels for arsenic.**
- **New Arsenic MCL is controversial due to high costs and uncertain health benefits.**
  - **Estimated national annual costs of implementing 10 ppb MCL range from $165M to $605M to save 7 – 33 lives**
  - **About 1 life/500,000 exposed persons per year**

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Radionuclides in drinking water

Uranium and its radioactive daughters (radium and radon) are also high and variable in Southwest drinking water

- **Treatment costs to comply with standards for As, Ra and U will be even higher for some communities.**
- **Systems that can remove several contaminants (e.g. arsenic and radium) will be most cost-effective for communities and should be considered when selecting technology for water treatment.**

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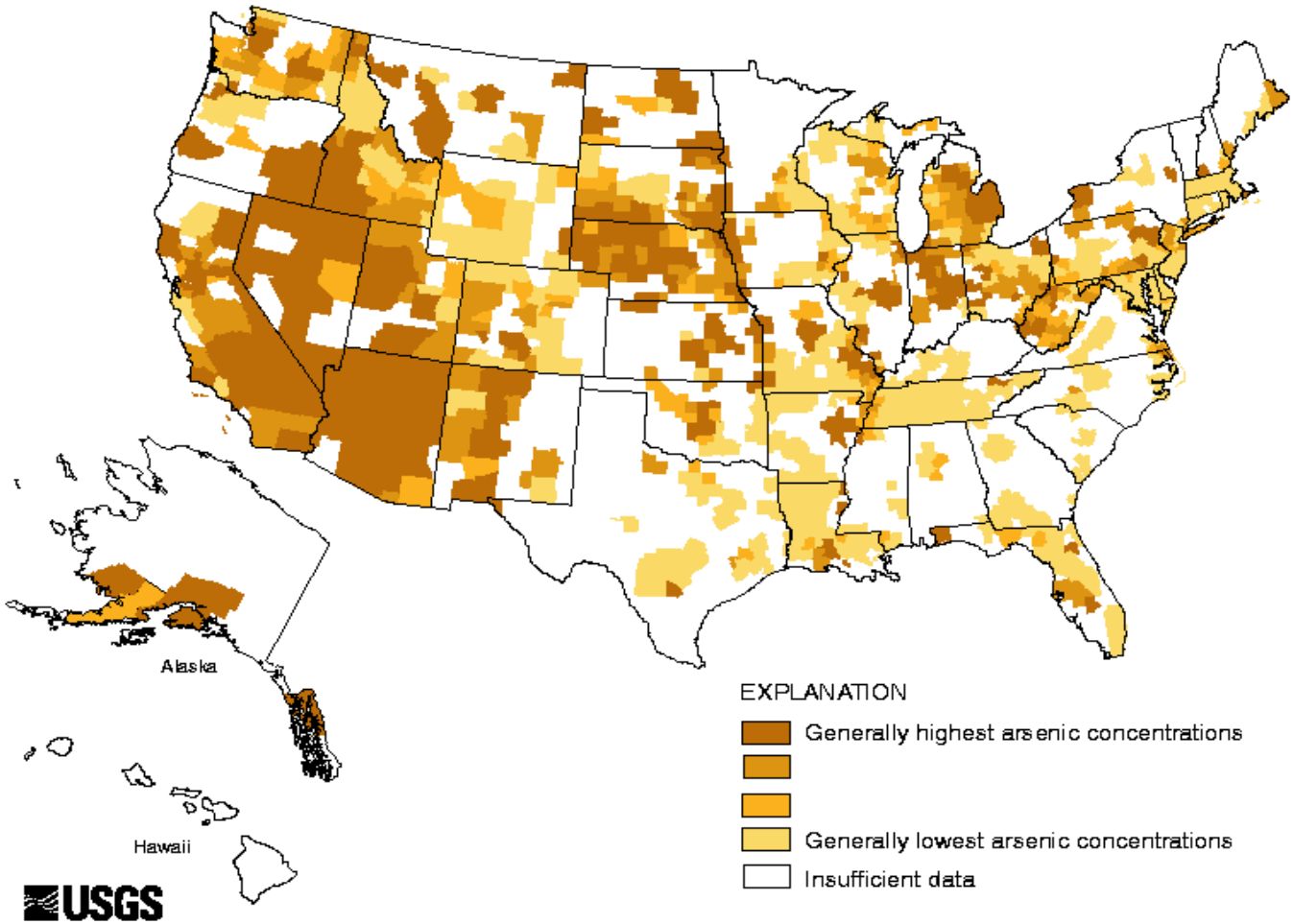
Arsenic Occurrence in the US



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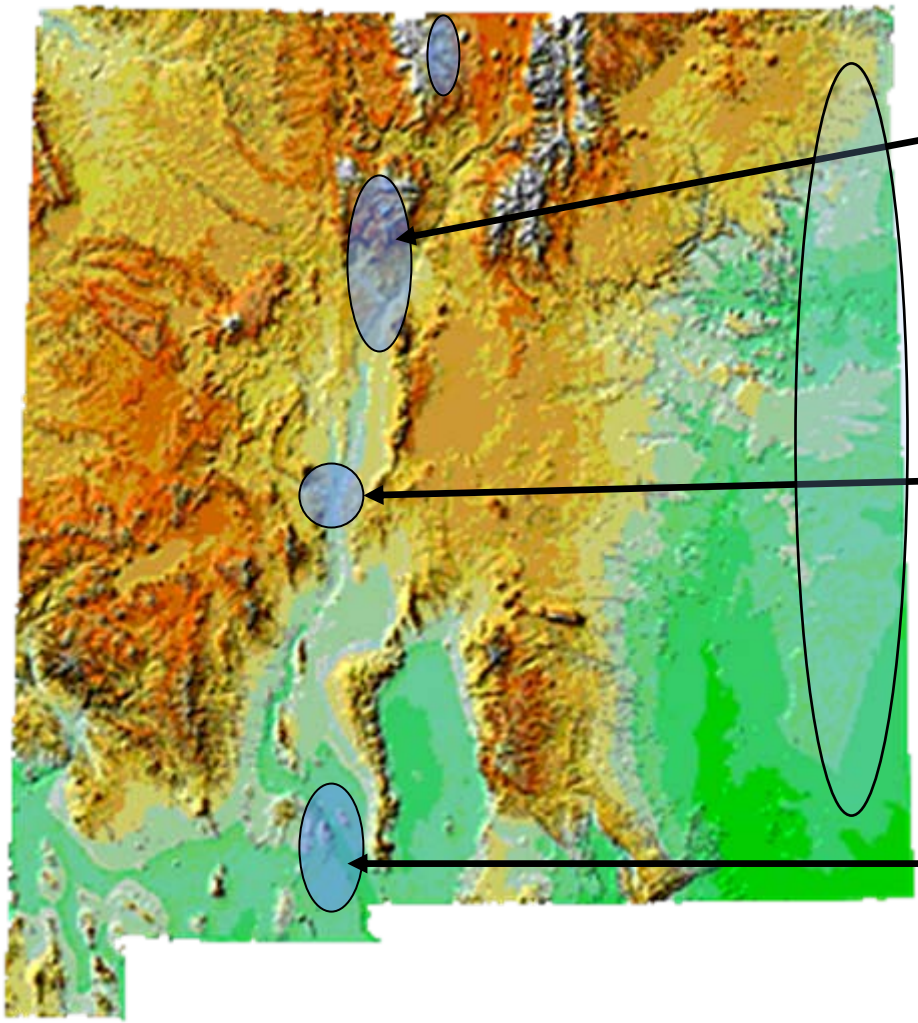
Sources of High Arsenic in New Mexico's Waters



- **Abundant in silicic volcanics**
  - **derived volcaniclastic sediments and associated hydrothermal systems**
- **Arsenic enrichment by Potassium Metasomatism**
  - **low temperature alteration common in closed hydrographic basins in arid climates**

Mixing of deep geothermal waters and shallower surface influenced waters

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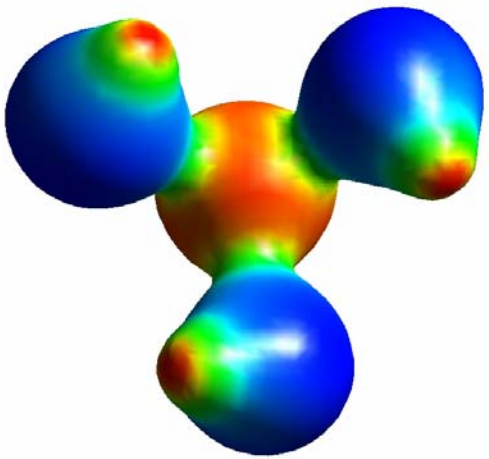
Arsenic Chemistry

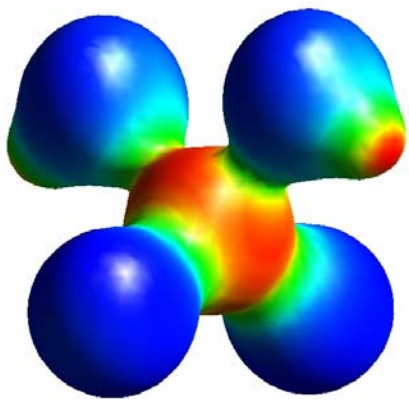


H_3AsO_3

Inorganic arsenic in groundwater usually exists as a combination of neutral As^{III} (arsenite) and anionic As^{V} (arsenate).

Arsenite is believed to be more toxic than arsenate.

$H_2AsO_4^-$



Arsenate is adsorbed by iron oxides more efficiently than arsenite and is more easily removed by conventional treatment methods.

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Chemical Processes Leading to High Arsenic in Natural Waters and Important in Treatment

- Reductive dissolution of iron oxides
  - co-release of adsorbed and structural As
- Reductive desorption of As(V)
  - strongly sorbed As(V) to weakly sorbed As(III)
- Competitive desorption
  - phosphate, bicarbonate, silicate, dissolved organics
- pH changes
  - increased pH leads to As(V) desorption

Health Effects of Concern for Arsenic

- **Bladder Cancer**
- **Lung Cancer**
- **Cardiovascular Disease**
- **Blackfoot Disease**

These are result of exposure to high doses over extended period of time.

Effects at low exposures at 10 – 100 ppb are uncertain.

Other effects of concern include diabetes, cancers of liver and kidney, birth defects

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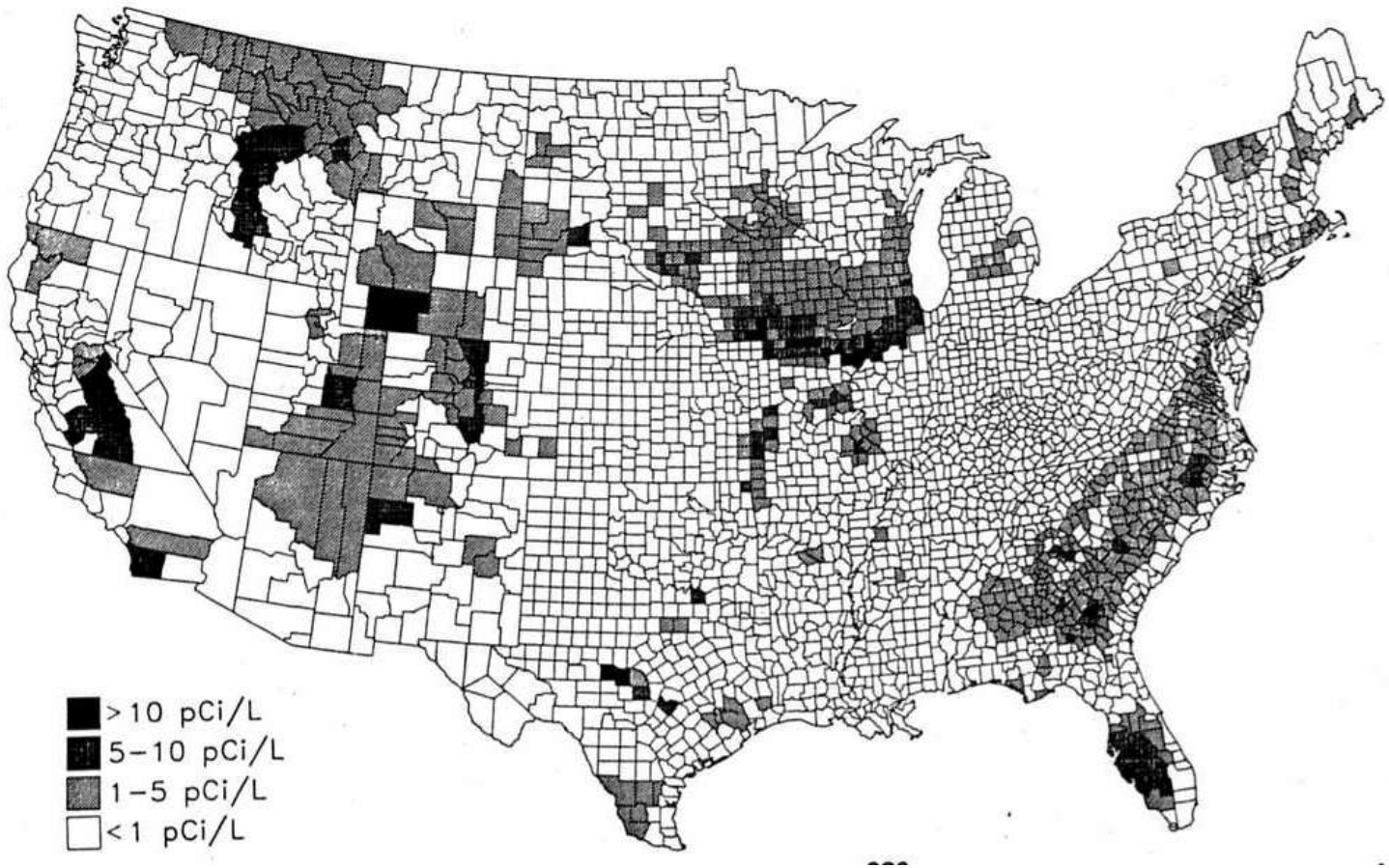
Ra-226 Occurrence in the US



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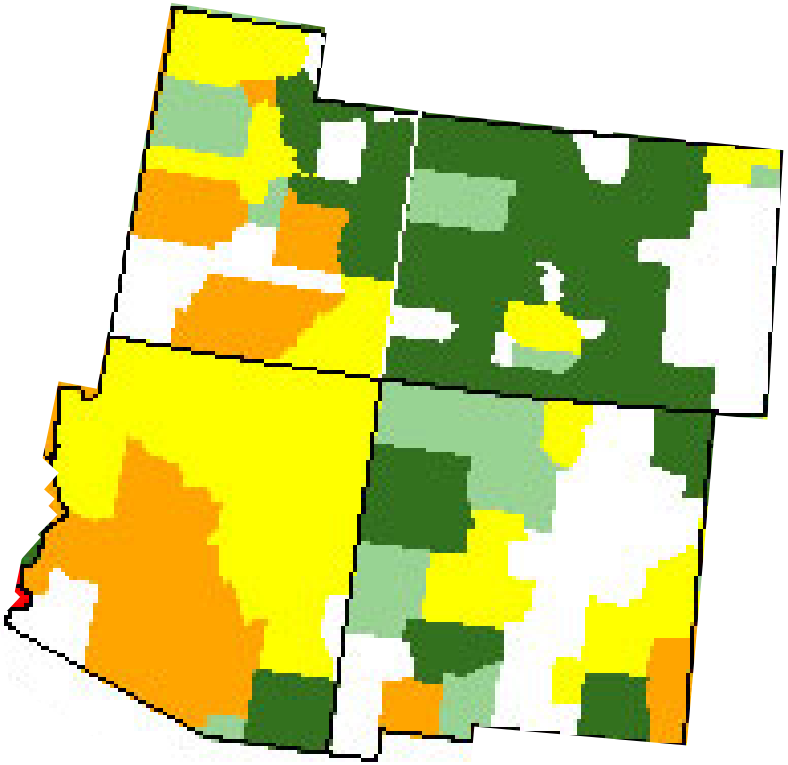
Geochemical Properties of Radium

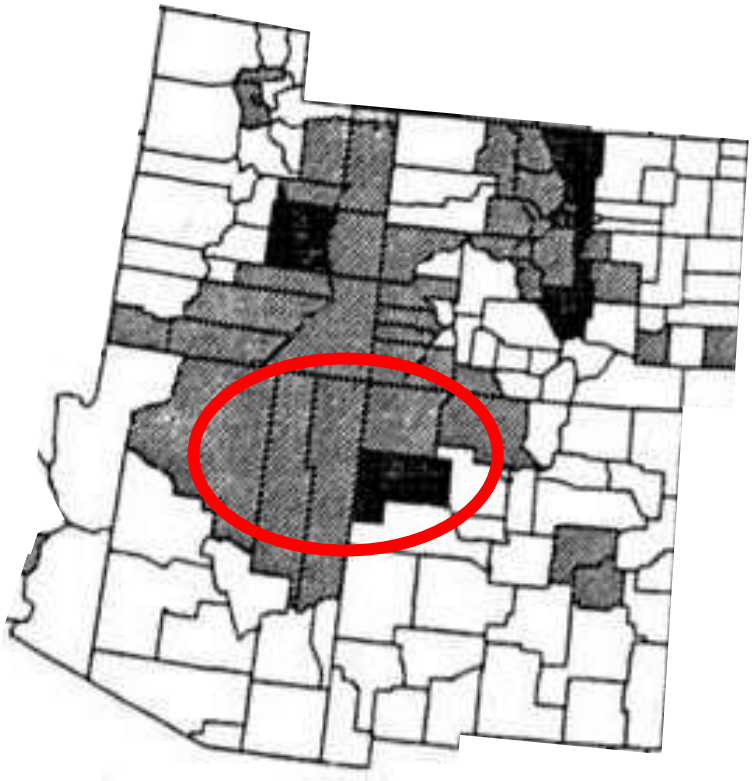
- **Ra-226: fifth member of U-238 series (α; $t_{1/2}$ = 1622y)**
  - **Distribution dominated by transport of soluble uranium parent**
  - **Concentration highest near enriched (reduced) uranium deposits.**
- **Ra-228: second member of Th-232 series (β; $t_{1/2}$ = 5.7y)**
  - **Distribution controlled by insoluble Th parent**
  - **Dominates in absence of secondary U enrichment**
- **Occurs as cation and is relatively insoluble but Ra-226 be solubilized by alpha-recoil.**
- **Radium levels highest in saline or reduced water due to low sorption by rock matrix (no Fe and Mn oxides).**

Health Effects and Radium

- **Biochemically similar to Ba and Ca; concentrates in bone when ingested.**
- **Increased risk of bone sarcomas, head carcinomas.**
- **Effects of oral ingestion demonstrated by studies of a large cohort of women who painted radium watch dials at beginning of century.**
- **Increased incidence of leukemia not observed but expected.**
- **Current regulation: $^{226}Ra + ^{228}Ra = 5$ pCi/L**

Arsenic and radium in the Southwest





25% As

- 10 µg/L
- 5 µg/L
- 3 µg/L
- 1 µg/L

Ave. Ra

- >5 pCi/L
- 1-5 pCi/L
- <1 pCi/L

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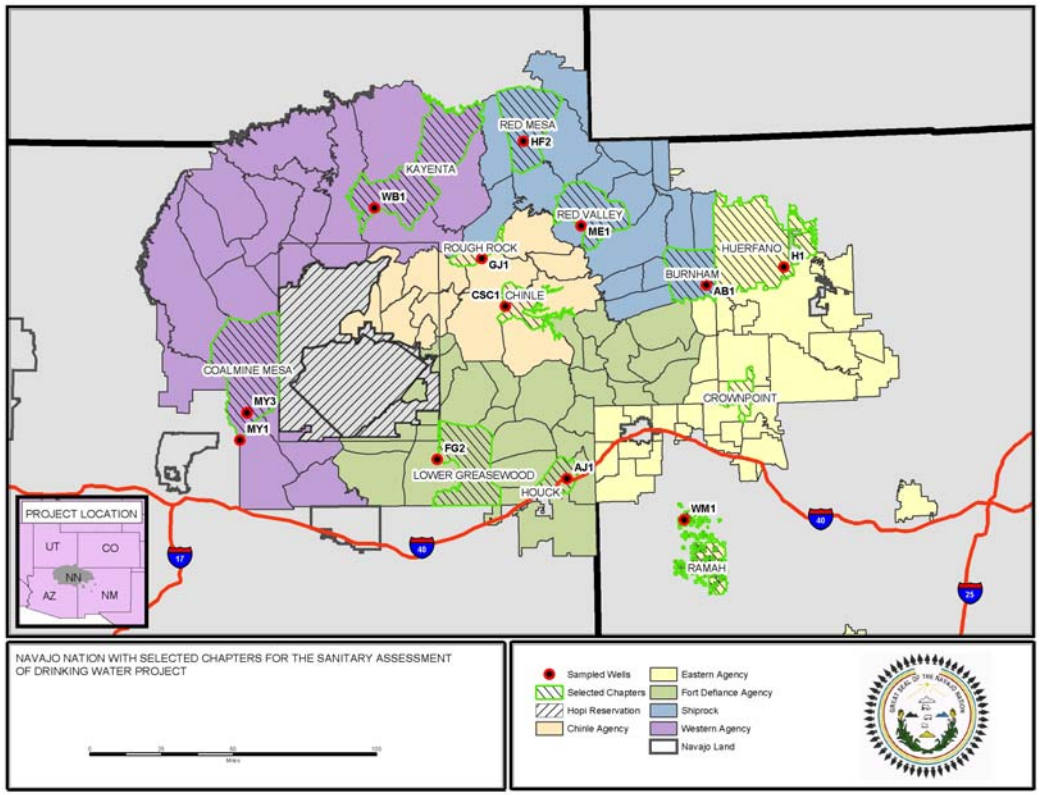
Collaboration with Navajo Nation EPA



AWTP goal: "40% of resources directed to rural and Native American utility needs"

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Arsenic Occurrence in Drinking Water Sources on the Navajo Nation

- **Public Water Systems Supervision Program under Navajo Nation EPA regulates approx. 166 public water systems (PWSs)**
- **Water sources of approx. 22 PWSs (13%) exceed Arsenic MCL of 10 ppb; some are Community Water Systems (CWSs) others are Non-Transient Non-Community Water Systems (NTNCWSs)**
- **Over 30% of Navajo residents are not connected to PWSs. Most of them haul water from unregulated water sources which contain contaminants such as arsenic, uranium, coliform and pesticides**

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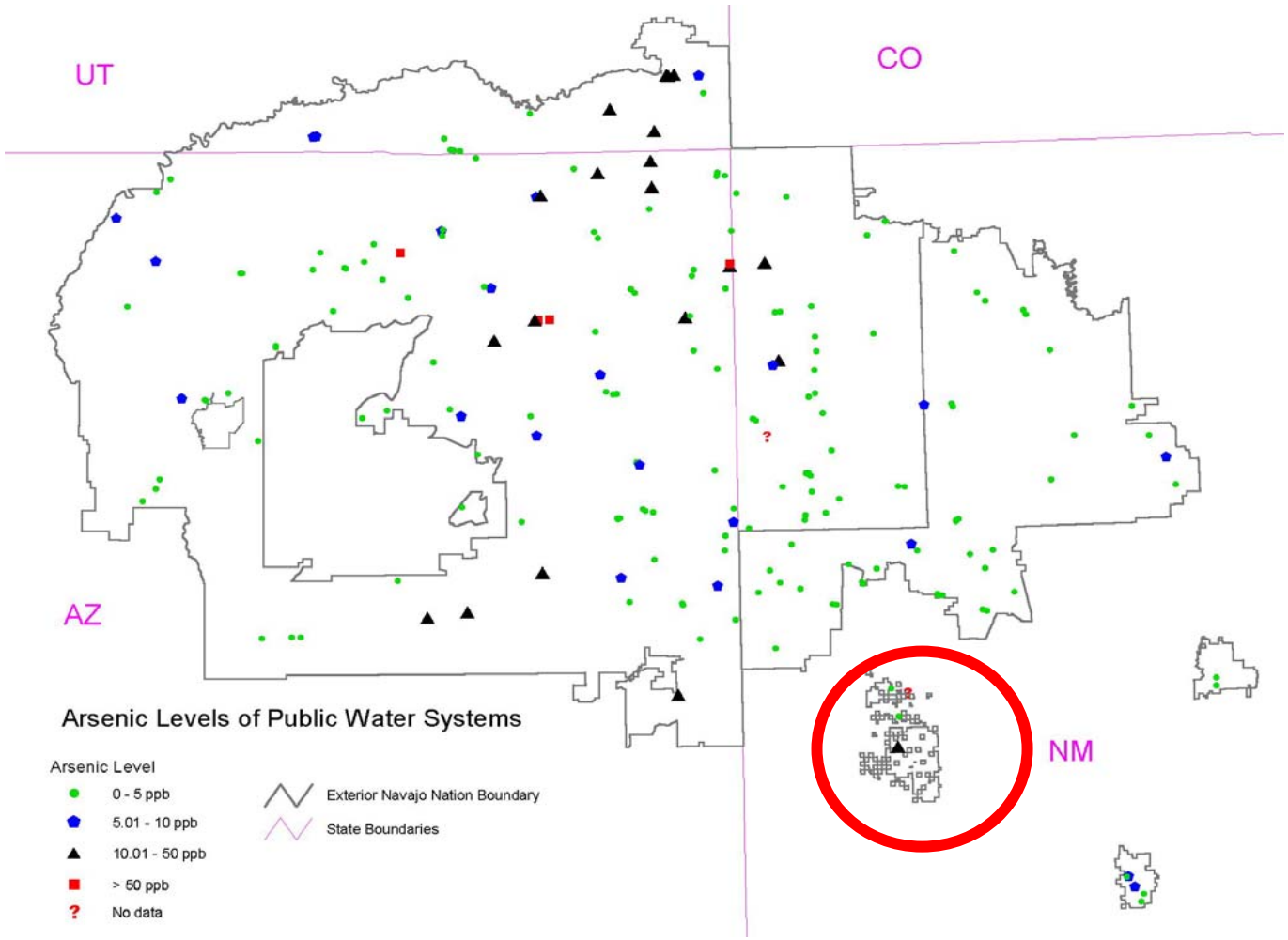
Arsenic Levels in Navajo Nation PWS Wells



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Outline

- Background:
  - Significance of multiple naturally-occurring contaminants in drinking water sources
- **Description of Pine Hill School site**
- Pilot Test
  - Objectives
  - Treatment technologies
  - Pilot skid design
- Preliminary Results
- Conclusions

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Pine Hill School, Ramah Navajo Reservation

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Pine Hill Water Quality

Red values exceed standards

	Well #2	Standard
As (ppb)- about 85% as As(III)	30	10
pH	7.8	NA
Gross alpha (^{230}Th pCi/L)	44.2	15
Gross beta (^{90}Sr pCi/L)	23.5	4 rem
Ra-226 (pCi/L)	12.0	Total = 5
Ra-228 (pCi/L)	2.3	
U (ppb)	2.9	30
SO_4^{2-}	302	250
Hardness as $CaCO_3$ ppm	146	NA

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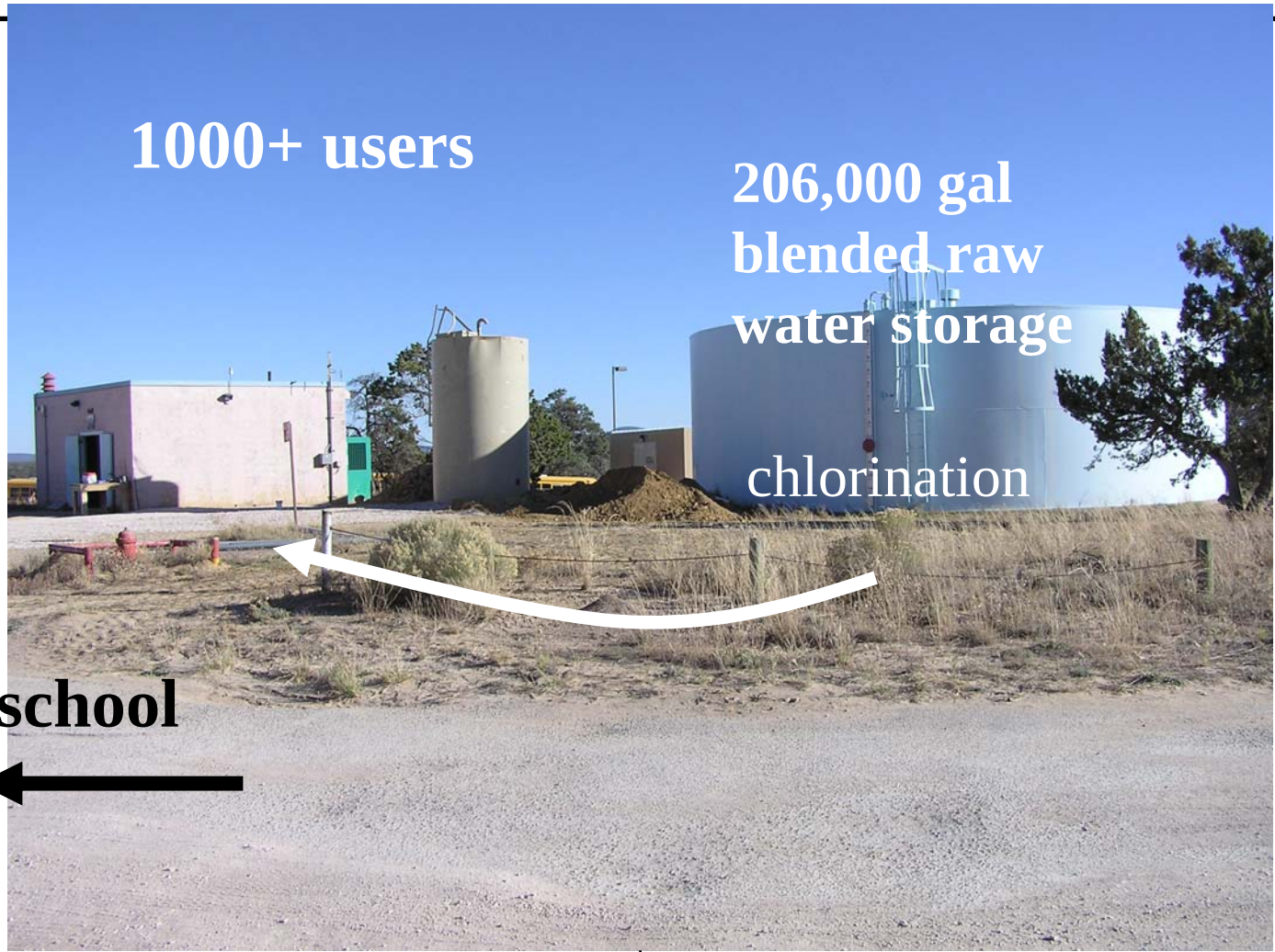
Pine Hill Water Treatment Plant



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Current system: iron removal

disinfection/fluoridation

Ra > MCL

Softening removes Ra

← iron removal

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Objectives of Test

- **Naturally-occurring radium in treated Pine Hill water supply above regulatory standards causes shut down of Well #2.**
  - **Community wanted to treat unblended water from the well for future growth and backup.**
- **Sandia National Labs (SNL) proposed to test innovative treatment technologies to augment or replace the current system at Pine Hill.**
  - **Results of test will help community choose new treatment system.**

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Roles and Responsibilities (I)

- **Vendors :**
  - **supply and set up test equipment systems at no cost**
  - **take samples and train Pine Hill operators for long term test.**
- **Pinehill utility :**
  - **water utility operators will perform operation checks, take water samples**
  - **Sample and pay for analysis of backwash and regeneration brines at contract lab.**

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Roles and Responsibilities (II)

- **Sandia National Laboratories:**
  - Coordinate test design and schedule with vendors and Pine Hill
  - Analyze water samples from normal operations
  - Interpret test results
  - Provide report to Pine Hill community
  - Provide services at no cost to community
- **Navajo Nation EPA:**
  - Assisted in site selection for pilot test
  - Review and approve safety plan, discharges into sanitary sewer
  - Conduct initial radiological surveys
  - Review final results and recommendations

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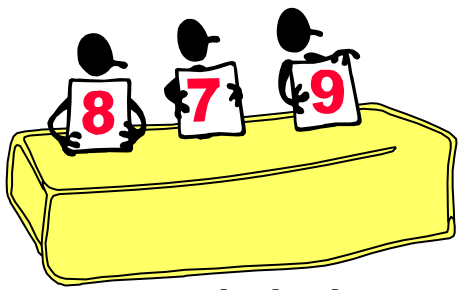
Additional Test Objectives

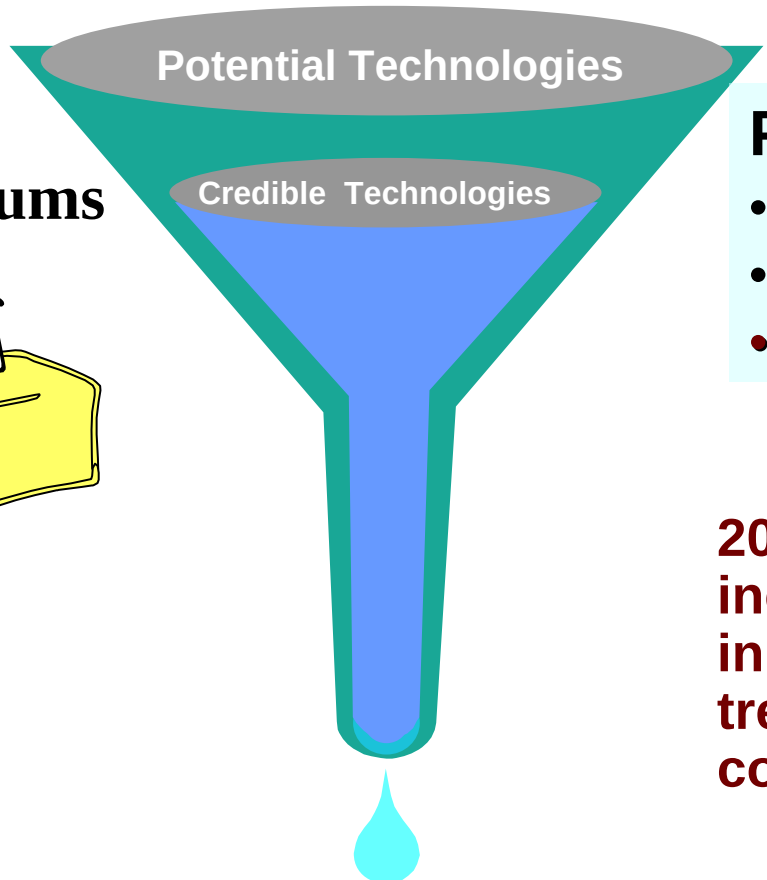
- Challenge adsorptive media with As(III)
- Compare adsorptive media to Coag/filtration
- Evaluate rapid low-cost analytical techniques for analysis of radionuclides at low levels relevant to regulations
  - LSC technique for gross alpha analysis
  - 3M Empore disks for radium analysis
  - Compare results to EPA-certified lab (GEL)
- Identify potential technologies of Point-of-Use systems for of population not on PWS in Pine Hill (36%) and remote parts of reservation (30%)

SNL Pilot Technology Selection Process

Vendors Forums



Technical Evaluation Teams



Suggested Pilot Technologies

Pool of technologies

- Vendors
- Universities
- Government labs

2005 Vendors Forum led to included evaluation of innovative technologies for treatment of multiple contaminants.

Report available!

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Selected Technologies

- **Calgon Carbon**
  - **CalMedia ™ GSR Plus synthetic granular manganese dioxide coated filter media**
    - **Addition of iron and manganese to assist in removal**
    - **Filter removes Fe, Mn, As, Ra and U**
    - **Backwash to sewer**
- **McPhee/Purolite**
  - **Mixture of ion exchange resins for separate removal of arsenic and radium**
  - **Regeneration brines to sewer**
- **None of the treated water will be returned to the distribution system from the pilot**

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Material Used in Tests

Calgon CalMedia GSR Plus

ArsenX^{np}

Both materials are NSF/ANSI 61 certified safe for drinking water systems.

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Pilot Treatment Shed and Storage Tank Supplied by Pine Hill School Facilities

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Calgon Carbon Pilot System

Oxidation/filtration system

Starts Nov 6, 2006.

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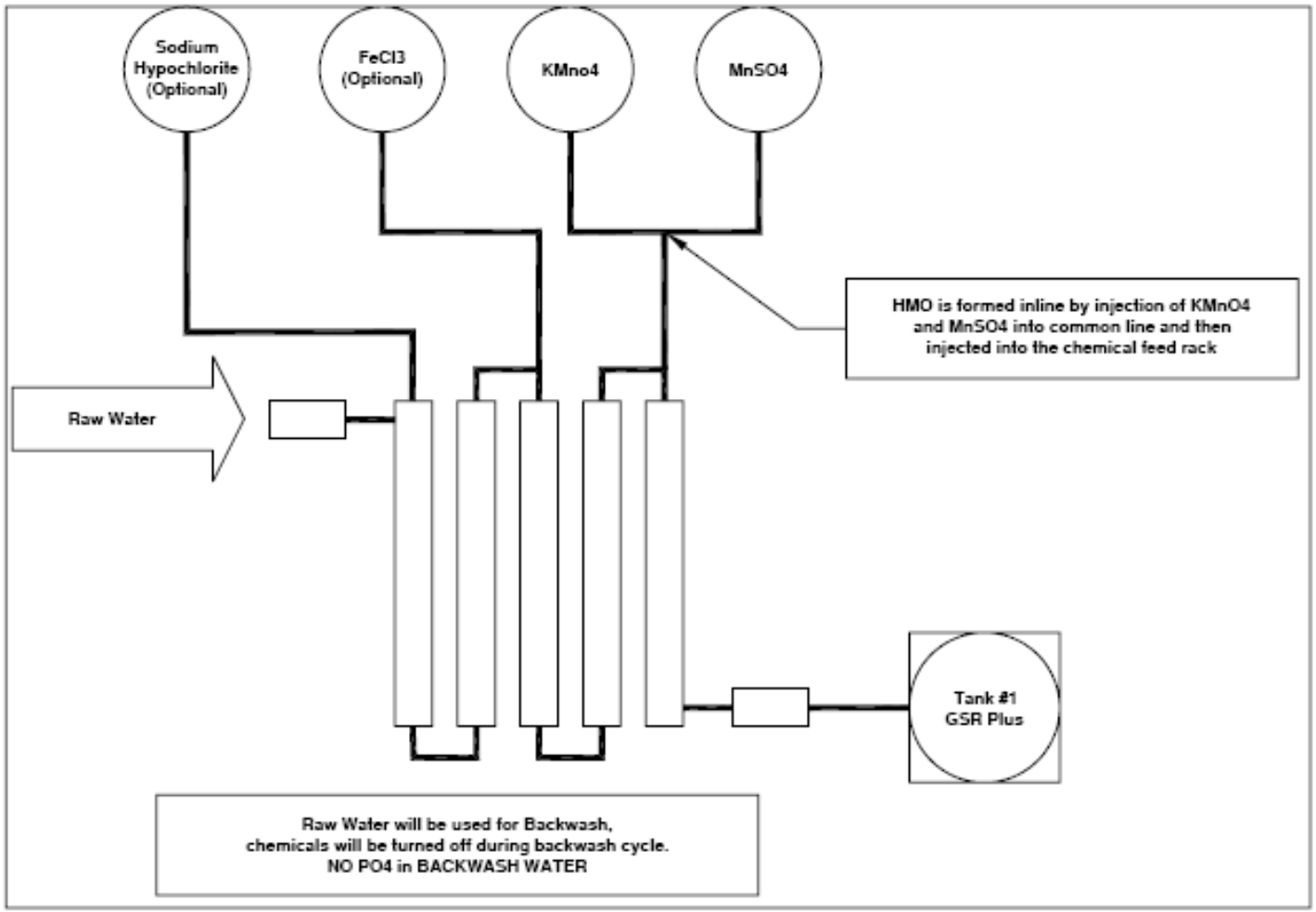
Calgon Carbon System



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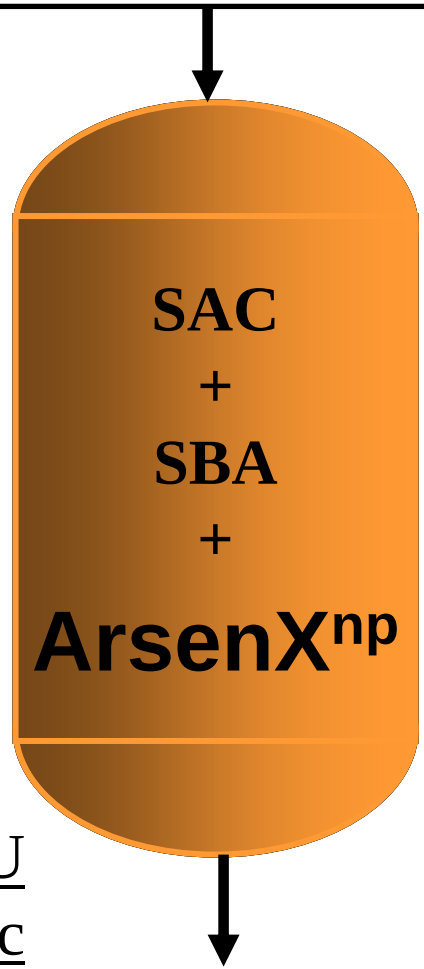
Adsorptive Media: McPhee/Purolite Resins

Combine removal of Cation

& Anion Contaminants:

- **Hardness**
- **Radium**
- **Arsenic**
- **Uranium**



Brine regenerate for radium, U
Alkaline regenerate for arsenic

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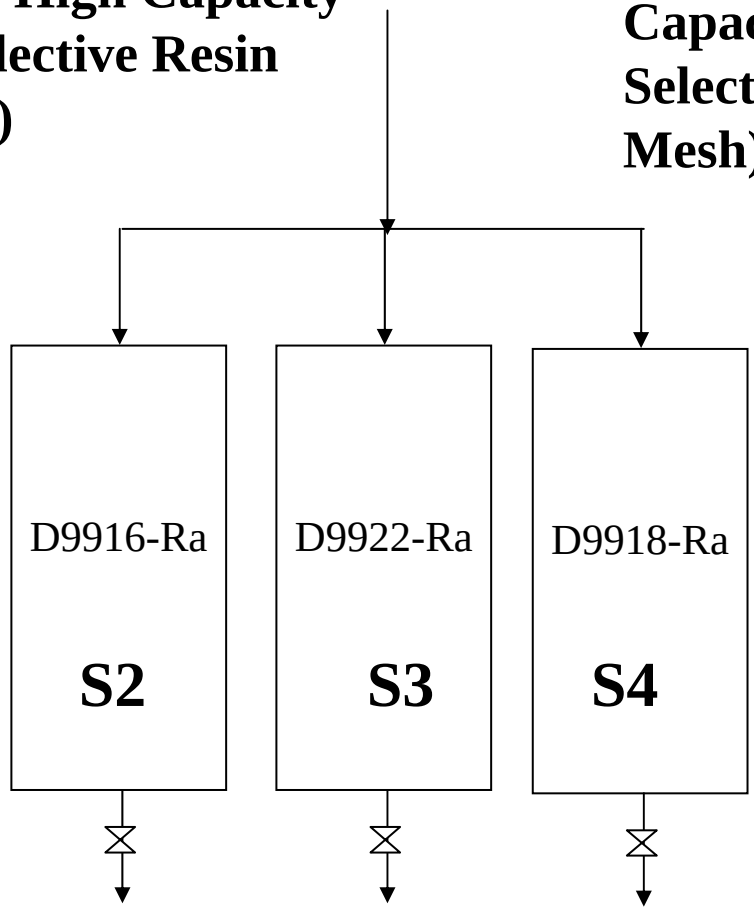
Test of Three Resins for Radium Removal

D9916 RS - High Capacity Radium Selective Resin (Single Use)

D9922 FM - High Capacity Radium Selective Resin (Fine Mesh) (Regenerable)



D9918-Ra - Shell-Core Resin - Radium/Hardness Removal (regenerable)- "Control"

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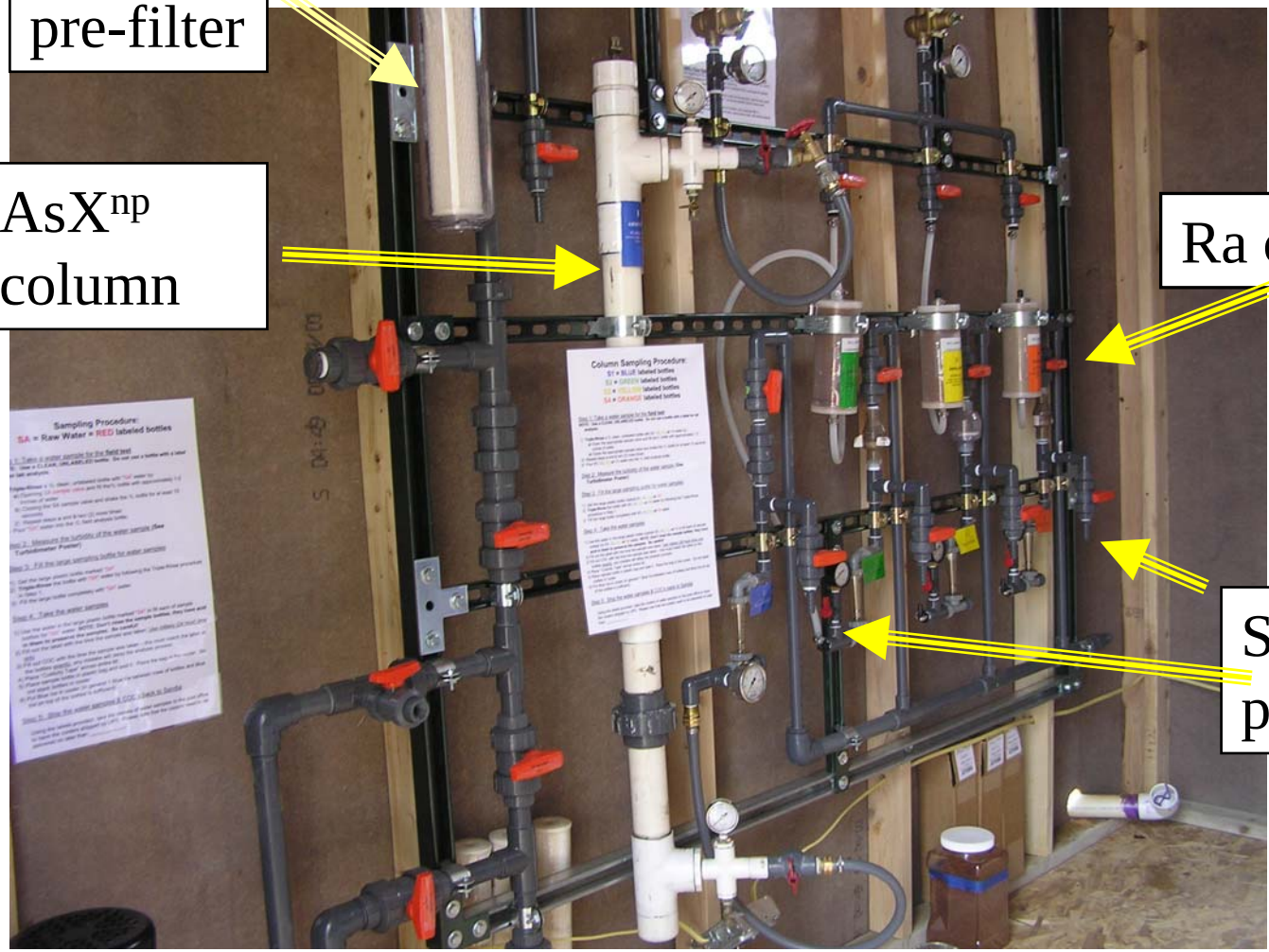
SNL Adsorptive media skid



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- Pilot Test
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- **Preliminary Results – data on 10/29**

  Test Still in Progress
- Conclusions

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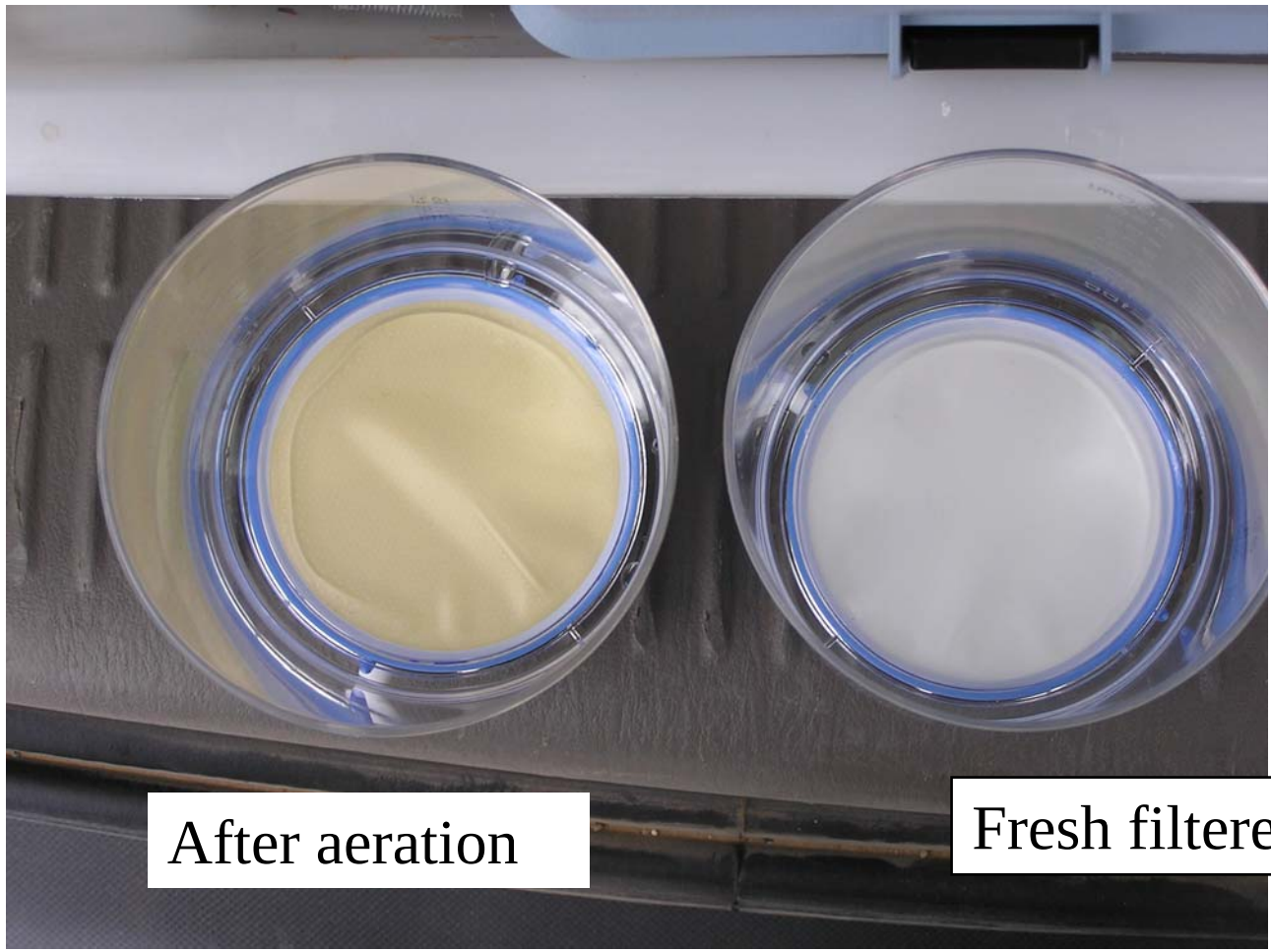
Source water is unstable



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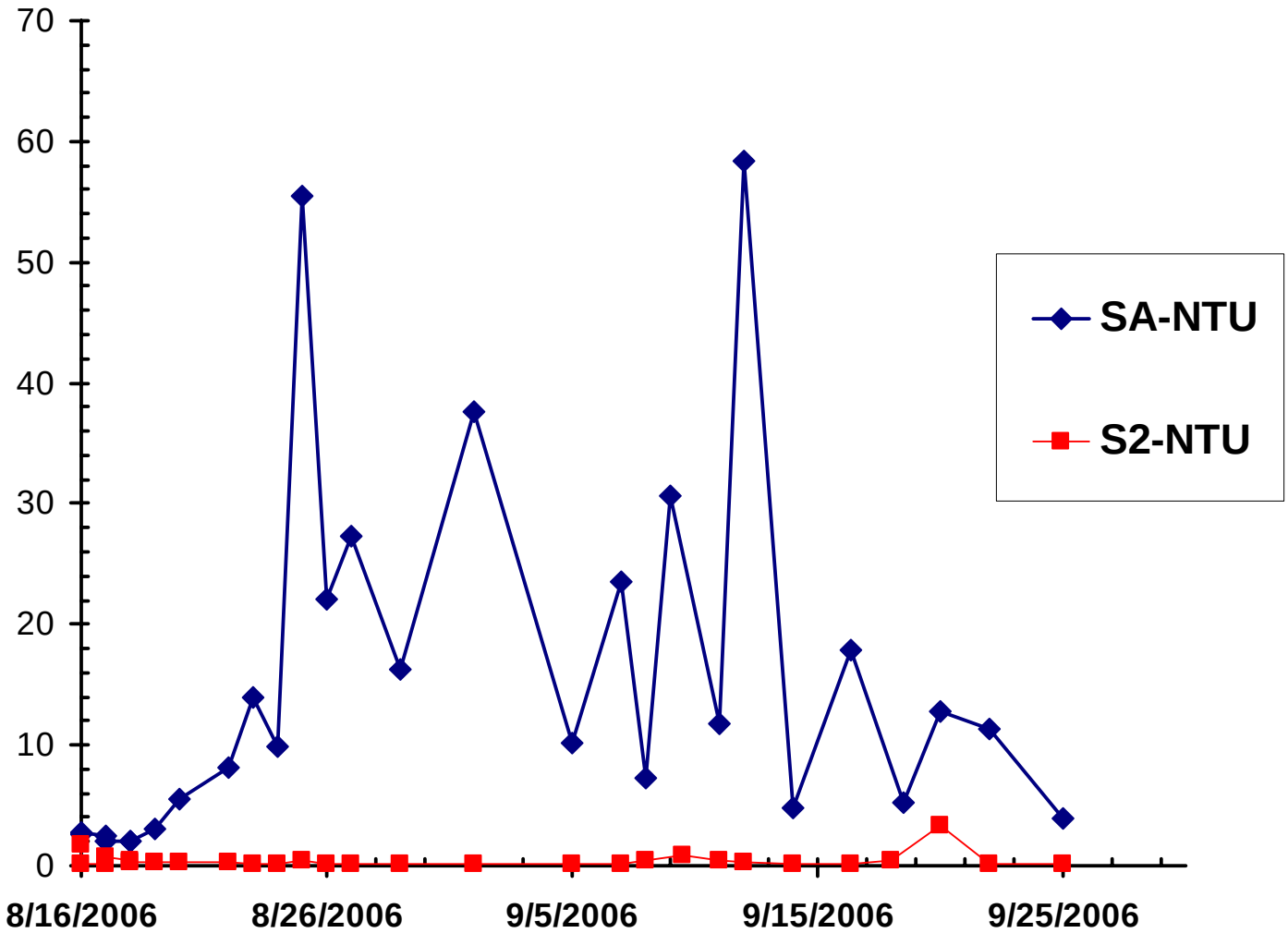
Turbidities of influent and treated waters



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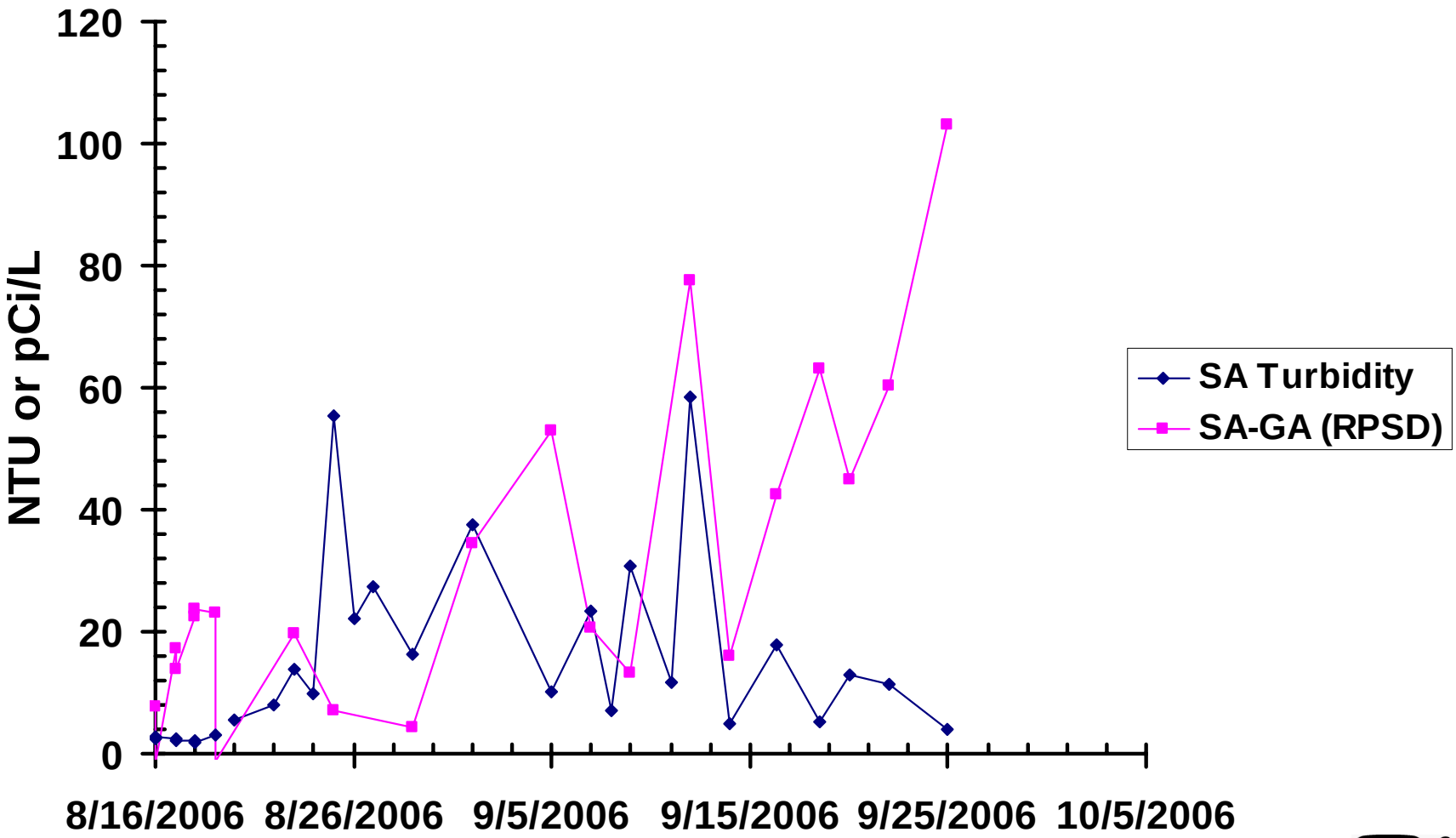
Turbidity and Gross alpha in influent water



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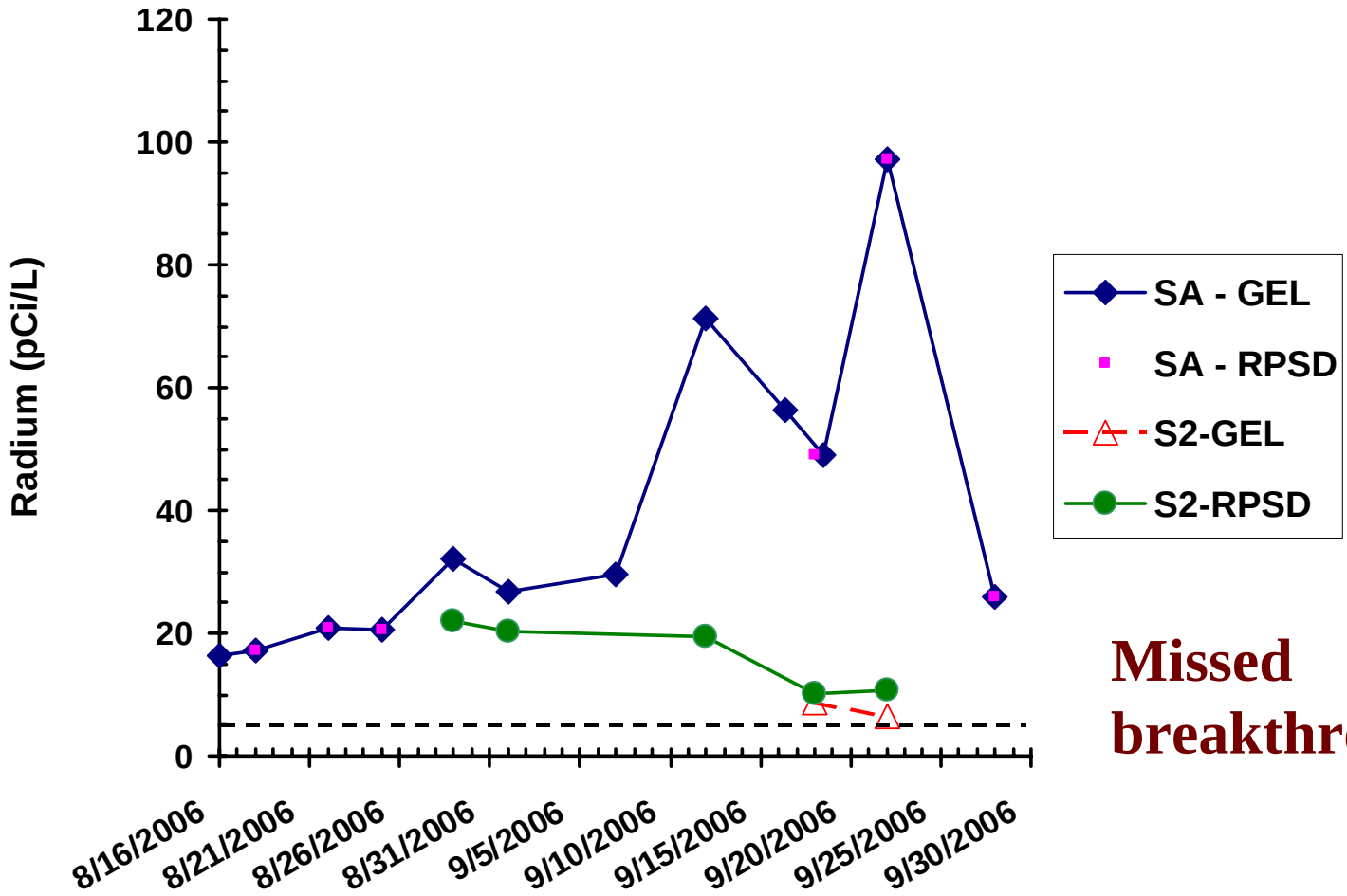
Radium removal by S2 Column



Missed breakthrough?

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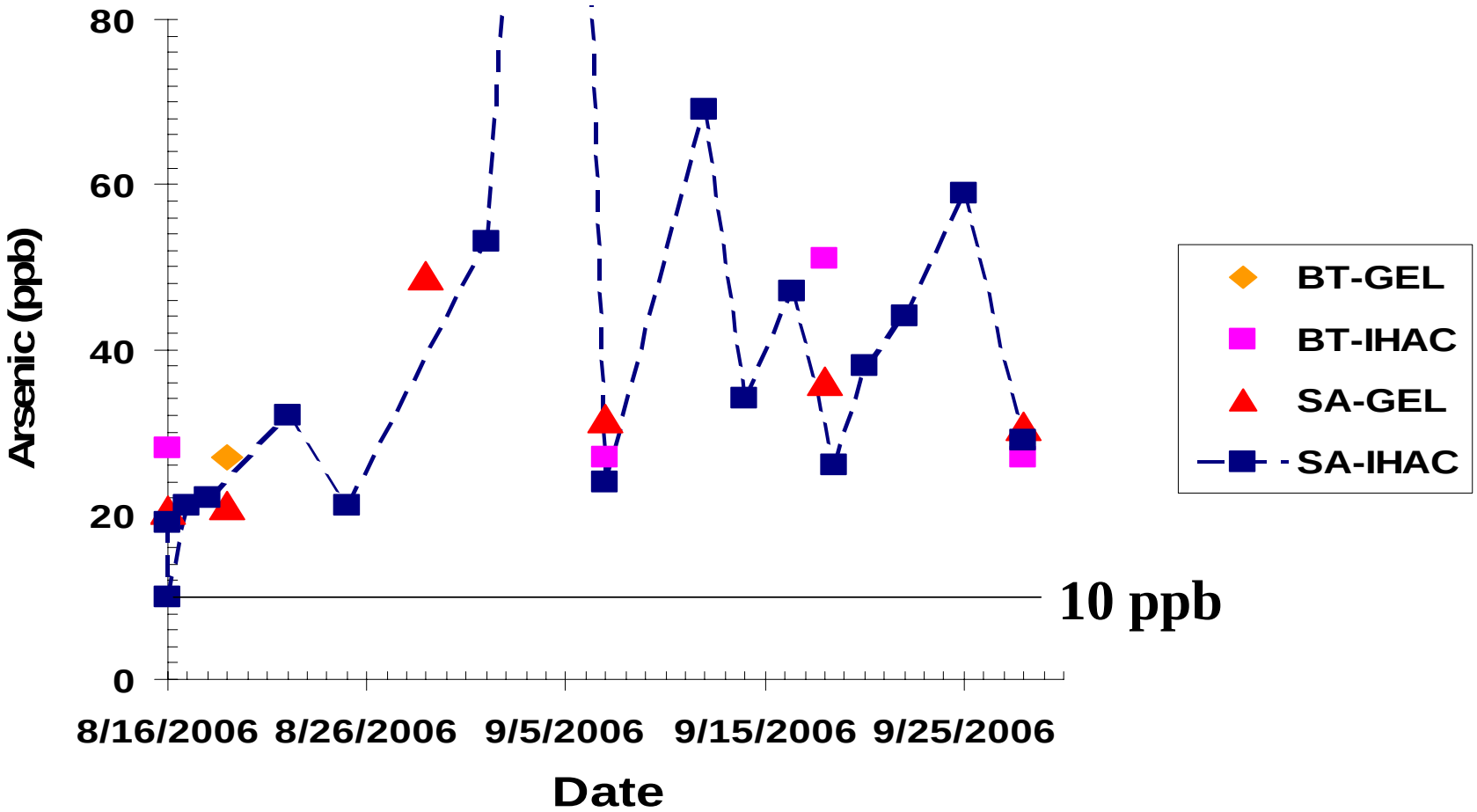
Influent Water Arsenic



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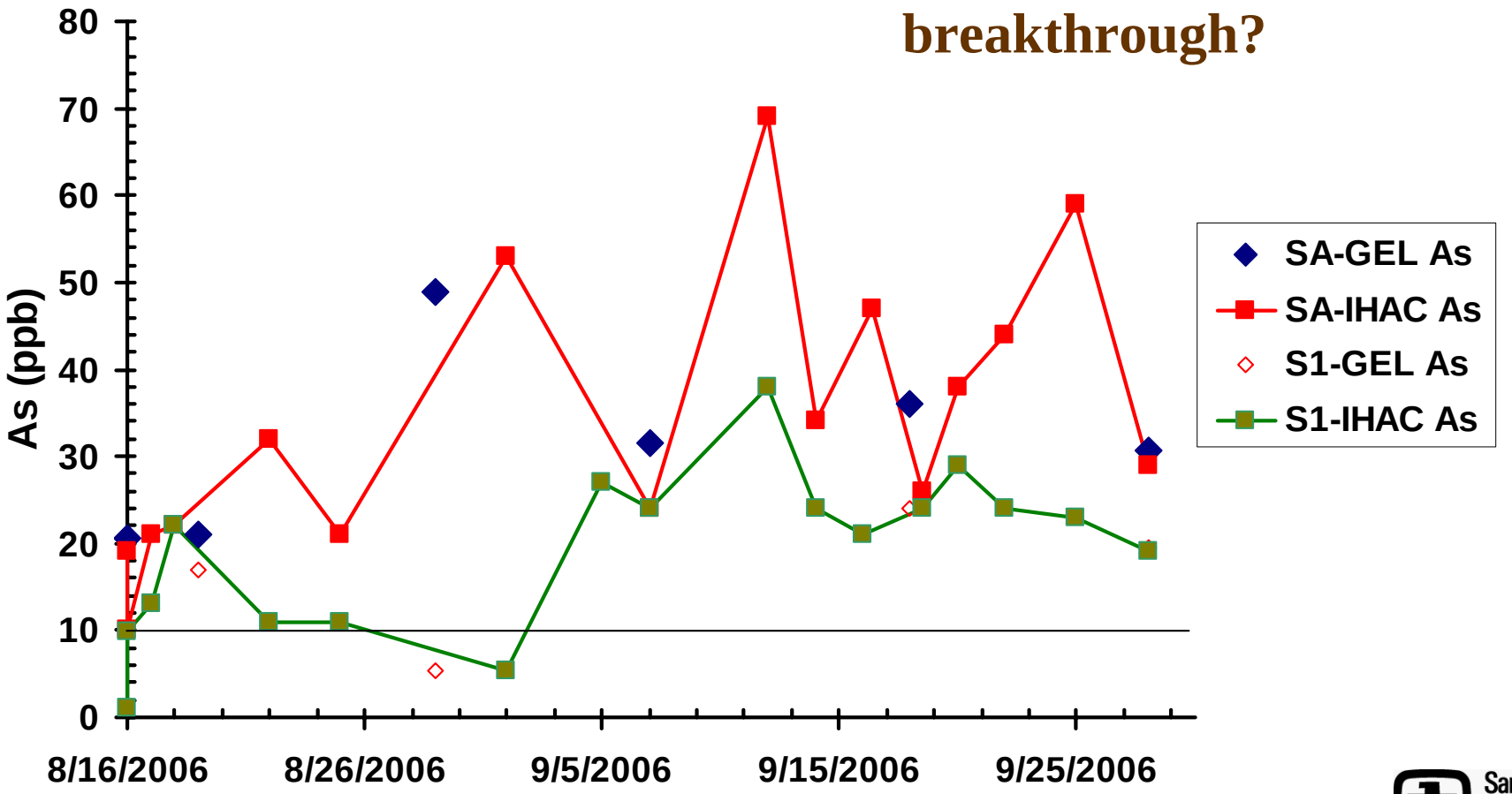
Arsenic removal by ArsenX^{np}

Reason for initial breakthrough?



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Preliminary results: Only bounds on breakthrough (days)

Treatment Column

COC	MCL	S1	S2	S3	S4
As	10 μg/L	6-10	NA	NA	NA
Ra^{26} + Ra^{228}	5 pCi/L	NA	<13	<30	3-6
Gross alpha	15 pCi/L	NA	>40?	>40?	10 -13

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Rough bounds on breakthrough (est. bed volumes)

Treatment Column

COC	MCL	S1	S2	S3	S4
As	10 μg/L	2600-4600	NA	NA	NA
Ra^{26} + Ra^{228}	5 pCi/L	NA	<9600	<22600	1900-4200
Gross alpha	15 pCi/L	NA	>30000 ??	>40000 ??	7300-9600

Preliminary Observations

- **Composition of influent water (SA) variable and dominates column performance**
  - **May reflect changes in source water during intermittent pumping cycle**
  - **May reflect changes in storage tank**
- **Columns not effective for first few days**
  - **Columns may need breaking in period.**
- **Low capacity of ArsenX^{np} for As(III)**
- **Additional verification of activity corrections needed.**
- **Water may be better suited to coagulation with filtration.**

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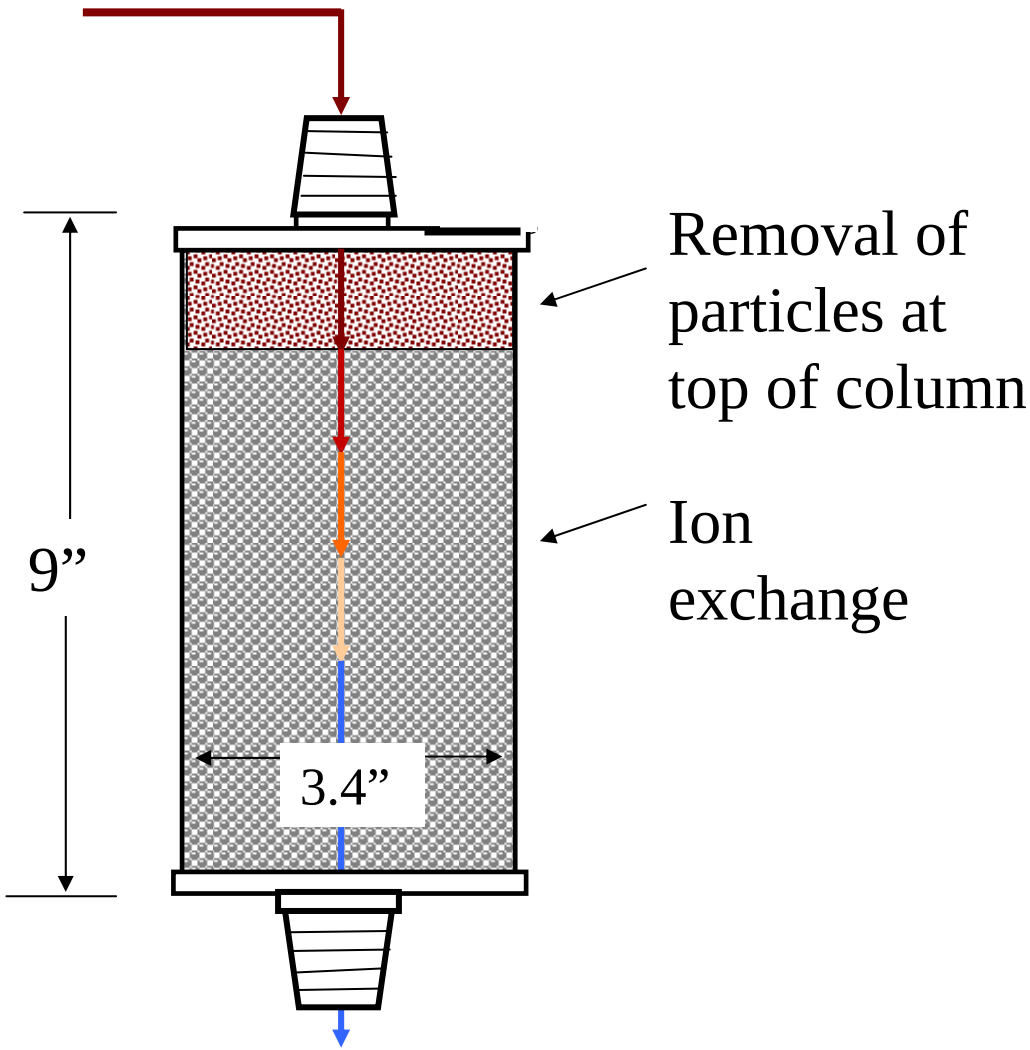
Removal of Contaminants by Filtration and Sorption



Radium columns

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Next Steps in Study

- Complete analysis of first adsorptive media test by end of 2006.
- Calgon Carbon test – Nov 6 – 15
- Phase II ArsenX^{np}
  - McPhee Engineering test
  - Pre-chlorination in rapid inline mixer
  - Expect higher capacity for As(V) compared to As(III)
- Pine Hill staff may evaluate other technologies before final selection

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POU Technologies for Water Haulers

- **Nationwide, more than 36,000 tribal homes lack access to safe drinking water.**
  - **More the 50% of these households are in Region 9.**
  - **New 10 ppb MCL for arsenic led to increase in systems out of compliance with SDWA.**
    - **20% of tribal water systems (100 systems) in Region 9 may be out of compliance.**
- **Water hauling imposes large financial burden on affected families.**
  - **5% of average household income ($1000)**
  - **NM Region 6 estimate: “up to $22,500/yr”.**
- **Over 30% of Navajo residents are not connected to PWSs, and many haul water from unregulated water sources.**
  - **arsenic, uranium, coliform and pesticides**
- **Can innovative point-of-use technologies be applied in areas not served by PWS on Tribal Lands?**

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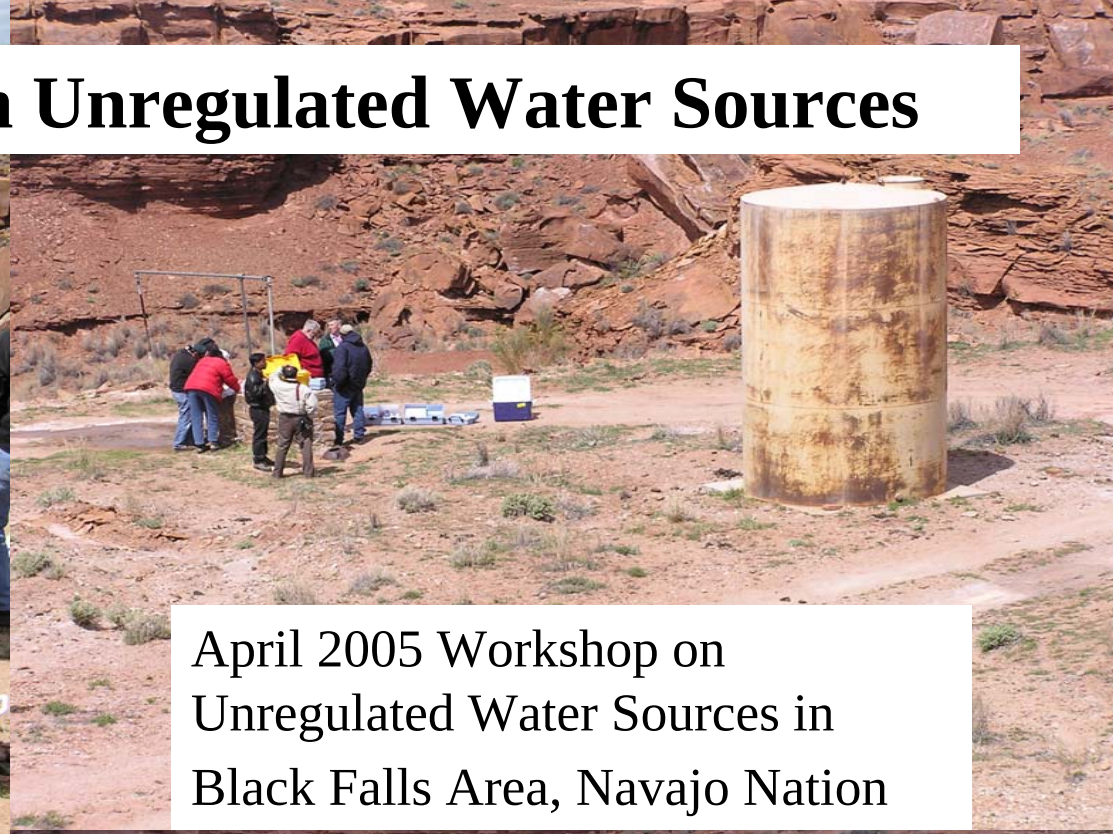
Early Interest in Unregulated Water Sources



April 2005 Workshop on Unregulated Water Sources in Black Falls Area, Navajo Nation

Need is well-recognized;

Funds to address it are lacking!

Box Spring

Poor access to safe drinking water is a world-wide problem

- **Between 1-2 billion people lack basic services**
  - **Unsafe drinking water is major cause of mortality and sickness in young children.**
  - **Water hauling imposes major financial and societal burdens on many people (especially women) in developing countries.**
- **Finding cost-effective (profitable) solutions to the problem has become a major objective of many large companies world wide. (e.g. Coca Cola, Procter& Gamble).**
  - **Explosion of Research and Development in water treatment technologies has resulted.**
- **Can studies in parts of Tribal Lands not on PWS help R&D for world-wide market?**

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Corporate Interest in Demonstrations on Tribal Lands

- **The Economic Drivers:**
  - **World-wide water treatment market**
  - **R&D Grants may require domestic application**
    - **Gates Foundation Grants, EPA SBIR?**
  - **Grainger Prize**
- **Companies expressing interest in workshop**
  - **Procter and Gamble – "C/F sachets"**
  - **Eagle Picher – coated diam. earth**
  - **Crystal Clear Technologies- treated zeolite/TiO_2**
  - **Luna Innovations (nanomagnetite)**
  - **Rohm and Hass- treated limestone**
  - **MIT – Kanchan Biofilter**
  - **NMT- laterite and sandstone**

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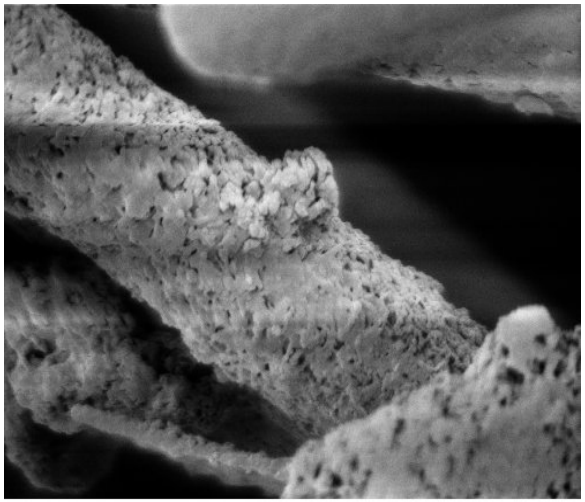
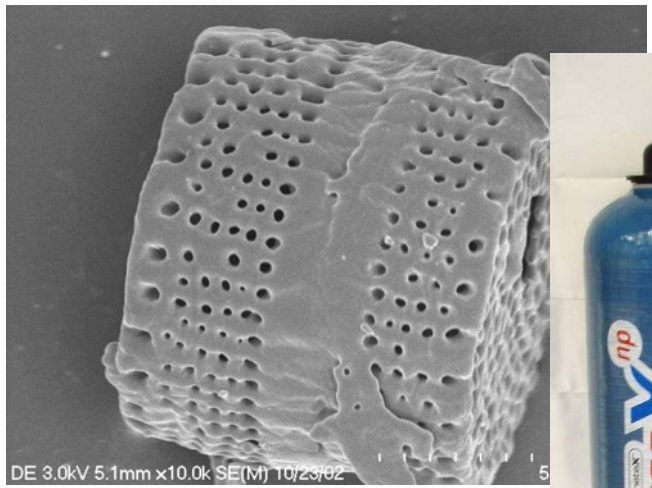
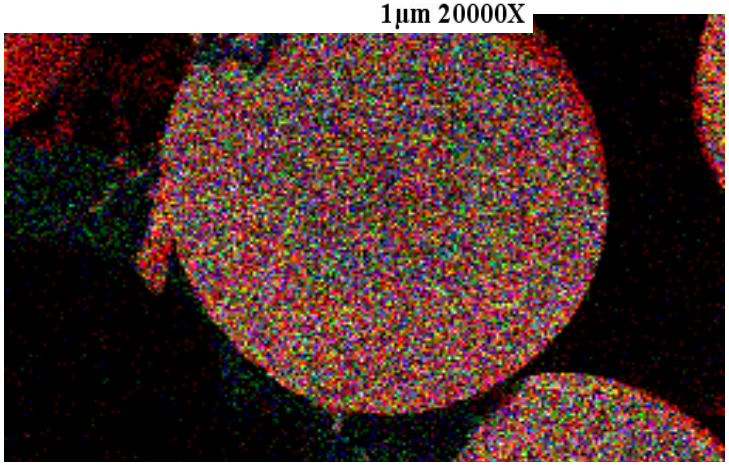
Treatment Using Engineered Nanotech Materials





1µm 20000X



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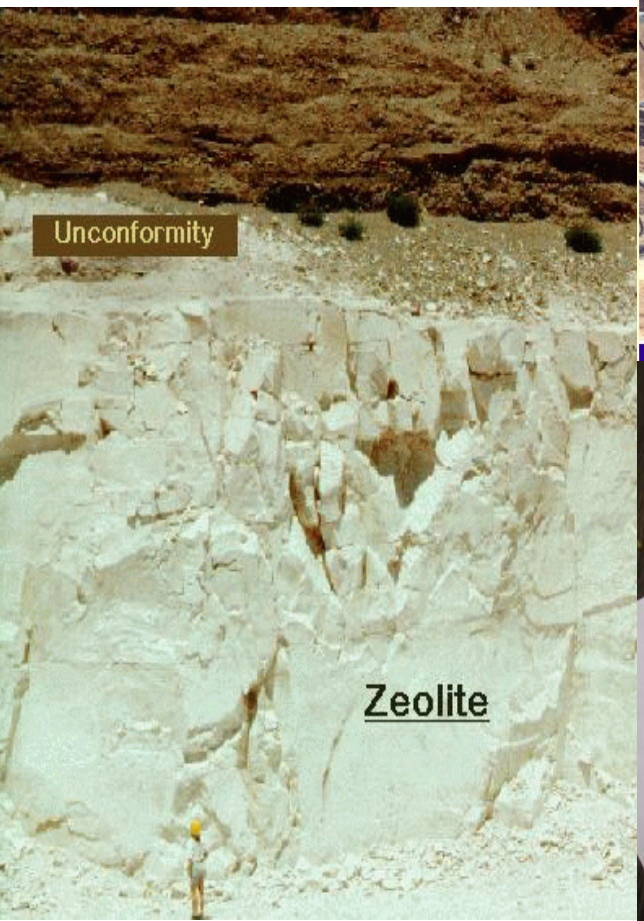
Treatment using low-cost natural materials



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Proposed Workshop - basic questions

- What are nature and magnitude of health effects associated with use of drinking water from non-regulated sources?
- Can point-of-use technologies developed for application in developing nations be applied in areas not served by PWS on Tribal Lands?
  - Regulatory barriers?
  - Technical barriers?
  - Social barriers
  - Economic Barriers

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Elements of Proposed Workshop

- Co-sponsored by interested agencies
- Invited expert speakers on major topics of health, occurrence, regulations, treatment technology overviews
- Vendor presentations on products (Forum)
- Supported primarily by in-kind services
  - Participants pay-their-own way
  - Hosted by participant agency
  - Charge registration fee to vendors?
- Use as spring board for future funded pilot studies with funding from several agencies.

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Summary

- **Pine Hill water presents challenges to conventional treatment technologies:**
  - **Hardness, radioactivity, As(III), hi Fe(II)**
  - **Arsenic, radium and sulfate levels are above regulatory standards.**
- **Collaboration between Sandia National Labs, Pine Hill Facilities and NNEPA provides basis for testing innovative treatment technologies to augment the current system.**
  - **Test designed to identify best commercially available technologies.**
- **Results may be applicable to other water systems with multiple contaminants**
  - **Desire to find technologies that can be used in POU applications in non-PWS in Navajo Nation.**

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Benefits to Pine Hill

"With the gained and/or acquired knowledge from the Pilot study we hope to utilize a technology from the Best Available Technologies (BATs) that will best treat the water for radionuclide's. "

"Thus far, Sandia National Laboratories in collaboration with the Navajo Nation EPA has provided an insight and a wealth of information in regards to the current situation with the use of the Pilot Study."

"During the course of the Pilot Study our location has been able to secure alternative funding through a proposal that will provide us the opportunity to utilize the acquired knowledge to develop a design and eventual construction to upgrade the current treatment plant with a filtration system that can maintain within the limits of the safe drinking water act (SDWA)"

- **Ward Hunter, Director Pine Hill Facility Department**

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- **Thank you for your interest.**
- **Project website**

http://www.sandia.gov/water/arsenic.htm

- **Questions?**

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